

SYNTHESIS AND SPECTRAL PROPERTIES OF CYANINE DYES BASED ON INDENO[2,1-*b*]CHROMENE

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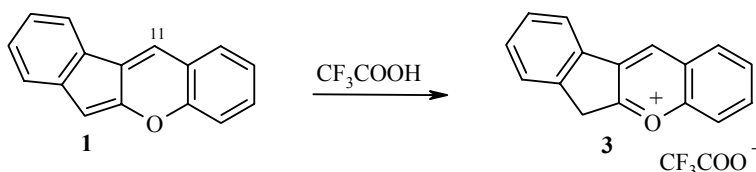
*Starting from the products of formylation and vinylformylation of indeno[2,1-*b*]chromene a series of new symmetrical and unsymmetrical polymethine dyes have been synthesized with a residue of indeno[2,1-*b*]chromene as the terminal group. It was shown that the unsymmetrical dyes obtained have two absorption bands in the visible region, the position, intensity, and shape of which depend on the nature of the second terminal group.*

Keywords: vinylformylation, pseudoazulenes, cyanine dyes.

Pseudoazulenes are π -isoelectronic analogs of azulene and are formally obtained by the replacement of a CH=CH fragment in the seven-membered ring of azulene by an O or S heteroatom or an NR group [1,2]. These systems retain an aromatic character and possess physical and chemical properties mainly analogous to azulene. The pseudoazulenes are of significant interest for synthesis and investigation of polymethine dyes, since they have characteristic absorption bands in the visible region [3-5], their fluorescence corresponds to a rare type of S^2-S^0 transitions [2, 6-9], and some of them display nonlinear optical properties [10].

Polymethine dyes containing pseudoazulene residues as terminal groups have not been investigated systematically up to the present time. Information in this area, in essence, is restricted to two studies, in which cationoid polymethine dyes of symmetrical [11] and unsymmetrical [12] structure, derivatives of 2,4-diphenyl-indeno[2,1-*b*]pyran, are described. In addition, a symmetrical monomethine cyanine, containing an indeno[2,1-*b*]chromene residue, is known [13].

The problem of the present work comprises the synthesis of new cyanine dyes having a residue of a pseudoazulene as terminal group and the study of their spectral properties. The system of the most available pseudoazulene, indeno[2,1-*b*]chromene (**1**), was selected for investigation [14]. There is information on the instability of 6H-indeno[2,1-*b*]chromenium perchlorate (**2**) preventing its isolation in the pure state [14], and also some data on salt **2**, obtained however on its incomplete protonation [15].



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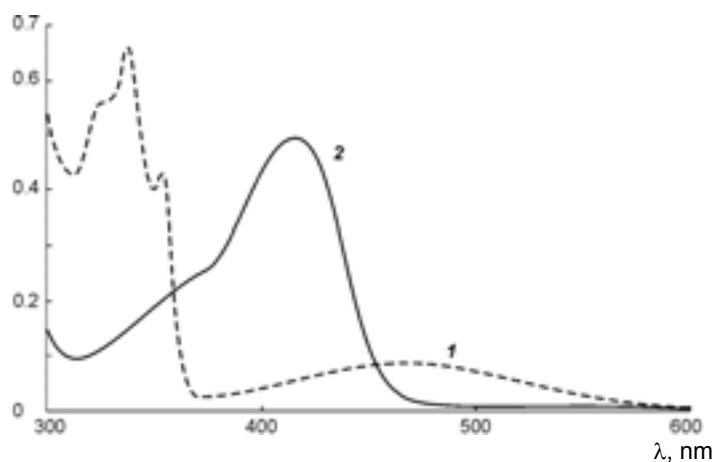
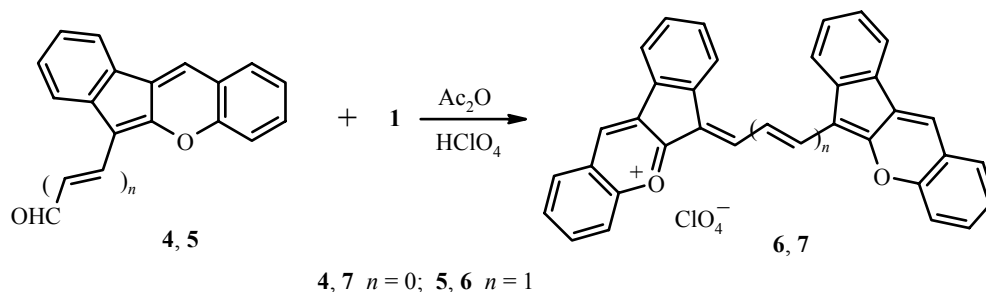


Fig. 1. Comparison of the absorption spectra of 1) indenochromene **1a** and 2) salt **2**.

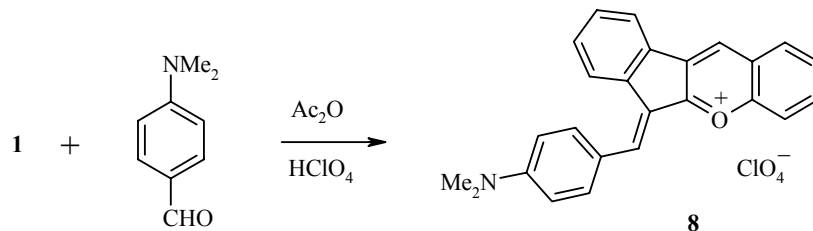
Comparison of the ^1H and ^{13}C NMR spectra of indenochromene **1** taken in DMSO-d_6 and of salt **3** obtained on treating it with CF_3COOD shows that protonation proceeds practically completely, and the chemical shifts and the character of the splitting of the proton signals are changed substantially. In particular the chemical shift of the H-11 proton is changed from 8.22 to 9.25 ppm, which indicates the change in the aromatic nature of the pseudoazulene to a benzopyrylium system. This conclusion is also confirmed by a comparison of the ^{13}C NMR spectra of the protonated and unprotonated forms. In compound **1** the signal at lowest field in the spectrum is at 152.2 ppm, and in the spectrum of salt **3** the signal at lowest field is at 183.1 ppm. The electronic spectrum of indenochromene **1** (measurement of the spectrum was carried out in MeCN in the presence of an excess of HClO_4) is changed in an extremely characteristic way. The absorption bands with maxima at 466 and 337 nm disappear and a new intense band appears with a maximum at 415 nm, which is similar to the absorption band of ordinary benzopyrylium salts (Fig. 1).

The target compounds were synthesized starting from indeno[2,1-*b*]chromene-6-carbaldehyde (**4**) and its vinyllog 3-(indeno[2,1-*b*]chromen-6-yl)-2-propenal (**5**). Compound **4** was obtained similarly to [13] by the formylation of indenochromene **1**. For the synthesis of the hitherto undescribed aldehyde **5** we used the known vinylformylation reaction of [16]. The interaction of indenochromene **1** with 3-dimethylaminoacrolein in acetonitrile in the presence of an equimolar amount of POCl_3 led to compound **5** in 96% yield.

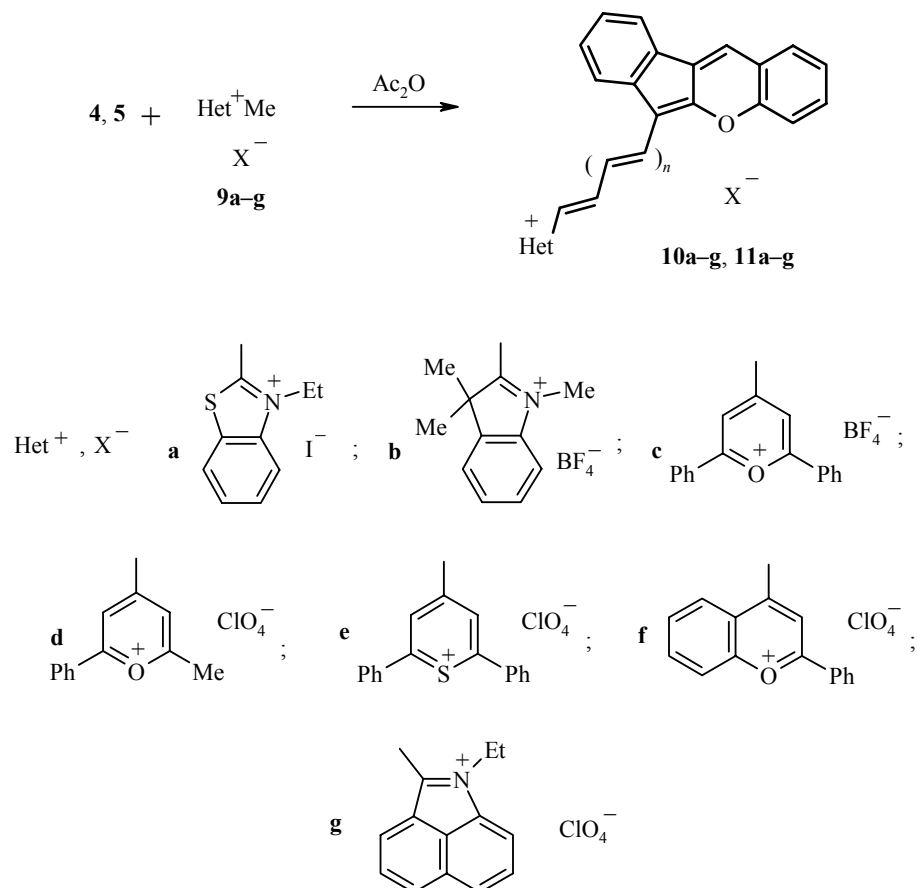
A trimethinecyanine of symmetrical structure **6** was synthesized by the condensation of aldehyde **5** with indenochromene **1** in acetic anhydride in the presence of HClO_4 . We note that in view of the low stability of the indeno[2,1-*b*]chromene salt **3** [14] it did not seem possible to obtain cyanine **6** in a one-stage condensation of this salt with the salt of malonic dialdehyde dianil as was done in the case of the symmetrical trimethinecyanine based on the nucleus of 2,4-diphenylindeno[2,1-*b*]pyran [11]. The symmetrical monomethinecyanine **7** was obtained for comparison of the spectral characteristics by the condensation of aldehyde **4** with indenochromene **1** under the same conditions [13].



The styrene **8** was synthesized by the interaction of indenochromene **1** with 4-dimethylamino-benzaldehyde.



The corresponding unsymmetrical cyanines **10a-g** and **11a-g** were obtained in good yield on carrying out the reaction of aldehydes **4** and **5** with the onium salts **9a-g**, which contain a reactive methyl group.



One band was observed in the visible portion of the absorption spectra of solutions in MeCN of the symmetrical dyes **6** and **7** and was located at 714 and 802 nm respectively. From a comparison of the absorption maxima of compounds **6** and **7** it follows that the vinylenic shift of the long wave band was 88 nm for them, which is somewhat less than the usual value (100 nm). This is probably caused by some steric hindrance existing in the monomethinecyanine **7** molecule which must lead to a bathochromic shift of its absorption bands [17]. Such a hypothesis is confirmed by modeling the compound **7** molecule by molecular mechanics.

There were two absorption bands in the visible region of the electronic spectra of the unsymmetrical dyes **10** and **11** (Table 1).

TABLE 1. Absorption Spectra of Solutions of Compounds **6**, **8**, **10**, and **11** in MeCN*

Compound	λ_1 (log ϵ_1)	λ_2 (log ϵ_2)	ϵ_2/ϵ_1	Compound	λ_1 (log ϵ_1)	λ_2 (log ϵ_2)	ϵ_2/ϵ_1
6	802 (4.64)	—	—	10g	710 (4.63)	522 (3.88)	0.179
7	714	—	—	11a	625 (4.39)	496 (4.39)	0.951
8	670 (4.45)	474 (4.29)	0.690	11b	599 (4.41)	502 (4.42)	0.809
10a	587 (4.35)	447 (4.48)	1.343	11c	760 (4.82)	546 (4.17)	0.221
10b	596 (4.36)	449 (4.44)	1.220	11d	707 (4.80)	—	—
10c	683 (4.62)	495 (4.11)	0.308	11e	778 (4.27)	—	—
10d	694 (4.56)	—	—	11f	717 (4.35)	565 (3.99)	0.140
10e	719 (4.75)	515 (4.02)	0.185	11g	795 (4.84)	551 (3.95)	0.079
10f	707 (4.81)	501 (4.01)	0.159		802 (5.05)	—	—
					787 (4.71)	—	—
					730 (4.73)	—	—

* λ is the wavelength at the maximum of the absorption band in nm, ϵ is extinction coefficient.

The ratio of the intensities of the long and short wave bands depends heavily on the nature of Het (Fig. 2).

For an electron-donating Het (**a** and **b**) two bands of close intensity are observed, but in the case of less electron-donating Het (**c-g**) the long wave band has a significantly greater intensity than the short wave. These features may be explained by the greater electronic asymmetry of compounds **10a,b** and **11a,b** than compounds **10c-g** and **11c-g** leading to a large localization of electron density in the indeno[2,1-*b*]chromene nucleus. For dyes **10a,b** and **11a,b** the short wave band is similar to polymethines and the broader long wave band to pseudoazulenes. In the case of the weakly electron-donating Het (**c-g**) the long wave band acquires the characteristic polymethine shape. On going over from carbocyanines to a dicarbocyanine of unsymmetrical structure a bathochromic shift is observed for the maxima of both absorption bands. The vinylenic shift of the

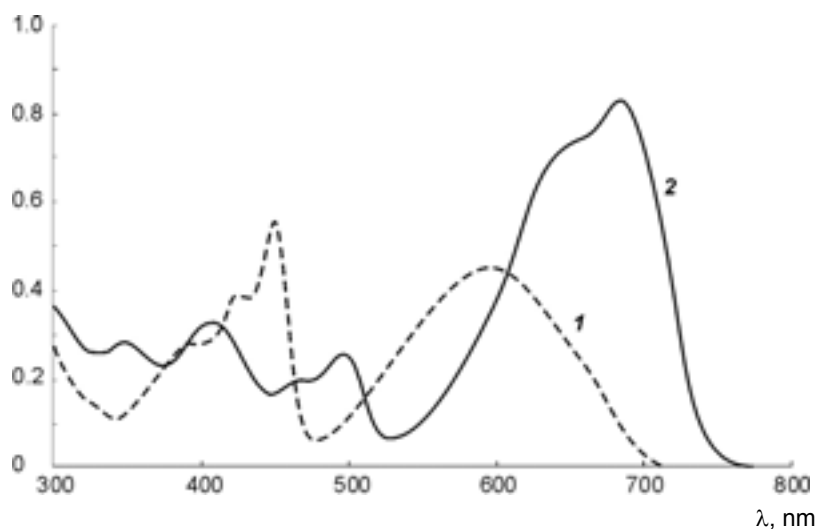


Fig. 2. Absorption spectra of 1) compounds **10b** and 2) **10c**.

short wave band for all the unsymmetrical dyes is ~50 nm, but the analogous shift of the long wave band depends on the electron-donating ability of Het. In the case of the more electron-donating Het (**a,b**) it was less and amounted to 40-60 nm but in the case of the less electron-donating Het it was greater at 75-95 nm, which approaches the vinylenic shift usual for symmetrical polymethine dyes. With a reduction in the electron-donating ability of the hetero residue (**c-g**) a tendency was observed towards an increase in the vinylenic shift.

Comparison of the absorption spectra of unsymmetrical dyes based on indeno[2,1-*b*]chromene with the absorption spectra of dyes based on indeno[2,1-*b*]pyran leads to the conclusion that there are similar regularities in the positions of the maxima, the shapes, and the intensities of the absorption bands of these dyes [12]. However, the introduction of an *ortho* phenyl fragment into the 2-methyl-4,6-diphenylpyrylium system of symmetrical dyes leads to a hypsochromic shift of the absorption band maximum [11] and the introduction of the same fragment into the 2-methylbenzopyrylium system of analogous dyes [18] leads to a small bathochromic shift of the maximum of this band.

It has therefore been shown possible to synthesize polymethine dyes with an indeno[2,1-*b*]chromene fragment as terminal group and a relatively short polymethine chain, absorbing in the near IR region. There are two absorption bands in the visible region of the spectra of unsymmetrical dyes, the absorption maxima and intensity ratios of which depend heavily on the nature of the second hetero residue. The nature of the absorption bands of polymethine dyes based on the indeno[2,1-*b*]chromene system is considered in more detail in [19].

TABLE 2. Characteristics of Compounds **6**, **8**, **10**, and **11**

Compound	Empirical formula	Found, % Calculated, %				mp, °C	Yield, %
		C	H	Hal	N (S)		
3b	C ₃₅ H ₂₁ ClO ₆	73.54	3.67	6.09	—	276-278	68
		73.37	3.69	6.19			
4	C ₂₅ H ₂₀ ClNO ₅	66.52	4.54	7.89	3.02	219-220	54
		66.74	4.48	7.88	3.11		
5a	C ₂₇ H ₂₀ INOS	60.83	3.84	23.89	2.60	179-181	62
		60.79	3.78	23.79	2.63		
5b	C ₂₉ H ₂₄ BF ₄ NO	71.02	4.95	15.68	(5.83)	272-274	71
		71.18	4.94	15.53	(6.01)		
5c	C ₃₅ H ₂₃ BF ₄ O ₂	74.85	4.09	13.33	—	292-293	65
		74.75	4.12	13.51			
5d	C ₃₅ H ₂₃ ClO ₆	73.12	3.89	6.15	—	223-225	40
		73.11	4.03	6.17			
5e	C ₃₅ H ₂₃ ClO ₅ S	71.21	3.98	5.97	(5.40)	>300	70
		71.12	3.92	6.00	(5.42)		
5f	C ₃₃ H ₂₁ ClO ₆	72.15	3.88	6.53	—	>300	79
		72.20	3.86	6.46			
5g	C ₃₁ H ₂₂ BF ₄ NO	72.78	4.50	14.73	2.87	258-260	81
		72.82	4.34	14.86	2.74		
6a	C ₂₉ H ₂₂ INOS	62.31	3.89	22.58	2.60	123-125	68
		62.26	3.96	22.68	2.50		
6b	C ₃₁ H ₂₆ BF ₄ NO	72.12	5.12	14.69	(5.69)	193-194	76
		72.25	5.09	14.75	(5.73)		
6c	C ₃₇ H ₂₅ BF ₄ O ₂	75.53	4.30	12.68	—	265-267	68
		75.53	4.28	12.91			
6d	C ₃₇ H ₂₅ ClO ₆	73.68	4.15	5.90	—	205-206	44
		73.94	4.19	5.90			
6e	C ₃₇ H ₂₅ ClO ₅ S	72.13	4.14	5.90	(5.18)	284-285	83
		72.01	4.08	5.74	(5.20)		
6f	C ₃₅ H ₂₃ ClO ₆	73.04	4.11	6.12	—	309-310	85
		73.11	4.03	6.17			
6g	C ₃₃ H ₂₄ BF ₄ NO	73.90	4.64	14.11	2.75	270-73	84
		73.76	4.50	14.14	2.61		

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Varian Gemini 300 (300 MHz) spectrometer, internal standard was TMS. The ^{13}C NMR spectra were obtained on a Varian Mercury 400 (100 MHz) spectrometer using J-modulation (APT). The electronic absorption spectra were recorded on a Shimadzu UV 3100 spectrometer.

Indeno[2,1-*b*]chromene (1) was synthesized by the known procedure of [14] from 2-indanol and salicylic aldehyde. ^1H NMR spectrum (DMSO- d_6), δ , ppm (J , Hz): 6.33 (1H, s); 7.19 (1H, t, $J = 8.4$); 7.3-7.6 (5H, m); 7.78 (1H, d, $J = 7.5$); 7.96 (1H, d, $J = 7.5$); 8.22 (1H, s, H-11). ^{13}C NMR spectrum (DMSO- d_6), δ , ppm: 97.4 (CH); 116.8 (CH); 120.0 (*ipso*); 120.2 (CH); 121.9 (CH); 122.2 (CH); 124.1 (CH); 124.4 (CH); 126.3 (*ipso*); 129.2 (CH); 129.9 (CH); 130.1 (*ipso*); 131.4 (CH); 141.5 (*ipso*); 151.0 (*ipso*); 152.2 (*ipso*). Electronic absorption spectrum (MeCN), λ_{max} , nm (log ϵ): 466 (3.34), 337 (4.22).

6H-Indeno[2,1-*b*]chromenium Trifluoroacetate (3). Indenochromene **1** (0.218 g, 1 mmol) was dissolved in trifluoroacetic acid (15 ml) at 20°C. The product was not isolated, using the reaction mixture for plotting spectra. ^1H NMR spectrum (CF_3COOD), δ , ppm (J , Hz): 7.35 (2H, m); 7.41 (1H, t, $J = 6.6$); 7.79 (2H, m); 8.06 (2H, m); 8.12 (1H, d, $J = 8.4$); 9.25 (1H, s, H-11). ^{13}C NMR spectrum (CF_3COOD), δ , ppm: 110.0 (CH); 113.0 (CH); 116.0 (*ipso*); 116.2 (CH); 120.2 (CH); 121.9 (CH); 122.2 (CH); 123.1 (CH); 123.7 (*ipso*); 126.7 (*ipso*); 127.0 (*ipso*); 130.0 (CH); 136.1 (CH); 147.9 (*ipso*); 183.1 (*ipso*). Electronic absorption spectrum (MeCN + excess HClO_4), λ_{max} , nm (log ϵ): 415 (4.09).

Indeno[2,1-*b*]chromene-6-carbaldehyde (4) was obtained by the method of [13] from indenochromene **1** (4.36 g, 20 mmol) and POCl_3 (3.98 g, 26 mmol) in DMF (30 ml). ^1H NMR spectrum (DMSO- D_6), δ , ppm (J , Hz): 7.33 (1H, t, $J = 7.5$); 7.47 (1H, t, $J = 7.5$); 7.55 (1H, m); 7.80 (2H, m); 7.98 (1H, d, $J = 8.1$); 8.09 (2H, t, $J = 9.0$); 8.77 (1H, s); 10.37 (1H, s).

3-(Indeno[2,1-*b*]chromen-6-yl)-2-propenal (5). A solution of POCl_3 (3.98 g, 26 mmol) in MeCN (10 ml) was added dropwise with stirring to a solution of 3-dimethylamino-2-propenal (2.57 g, 26 mmol) in MeCN (70 ml) cooled in an icebath. The mixture obtained was stirred for 15 min, then indenochromene **1** (4.36 g, 20 mmol) was added to it. The reaction mixture was stirred for 2 h, then left to stand for 24 h at room temperature. The MeCN was evaporated in vacuum and the residue rubbed under cold 10% NaOH solution. The solid was filtered off, washed several times with water, and recrystallized from MeCN. Product **5** (5.22 g, 96%) was obtained. ^1H NMR spectrum (DMSO- d_6), δ , ppm (J , Hz): 6.94 (1H, dd, $^3J = 15.6$, $^3J = 7.8$); 7.32 (1H, t, $J = 6.3$); 7.49 (2H, m); 7.65-7.85 (3H, m); 7.85-8.07 (3H, m); 8.54 (1H, s); 9.68 (1H, d, $J = 7.8$).

6-{3-(Indeno[2,1-*b*]chromen-6-yl)-2-propenylidene}-6H-indeno[2,1-*b*]chromenium Perchlorate (6). A mixture of aldehyde **5** (0.272 g, 1 mmol) and indenochromene **1** (0.218 g, 1 mmol) in acetic anhydride (10 ml) was heated to boiling, then cooled, 70% HClO_4 (0.1 ml) was added, and the mixture boiled for 5 min. The solid precipitated after cooling was filtered off, washed with ether, and recrystallized from 2-nitropropane.

6-[1-(4-Dimethylaminophenyl)methinyl]-6H-indeno[2,1-*b*]chromenium Perchlorate (8) was obtained analogously to perchlorate **6** from indenochromene **1** (0.436 g, 2 mmol) and 4-dimethylamino-benzaldehyde (0.298 g, 2 mmol), and was recrystallized from 2-nitropropane.

Cyanines 10a-g, 11a-g (General Method). A mixture of aldehyde **4** or **5** (1 mmol) and salts **9a-g** (1 mmol) in acetic anhydride (10 ml) was boiled under reflux for 5 min. After cooling, solid products **10** or **11** were precipitated, and were filtered off, washed with ether, and recrystallized from 2-nitropropane

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